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⑪ Publication number: 0 411 461 B1

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## EUROPEAN PATENT SPECIFICATION

⑯ Date of publication of patent specification: 18.10.95 ⑮ Int. Cl. 6: C08G 18/38, C08G 18/80,

⑯ Application number: 90114263.8 C08G 18/79, C08G 18/76,  
D21H 13/20, C08G 18/02,

⑯ Date of filing: 25.07.90 C08G 18/08, C08G 18/32,  
D01F 6/76

⑯ Hydrophilic polycarbodiimide polymer, pulp-like material consisting of said hydrophilic polycarbodiimide polymer, and process for producing said polymer or said material.

⑯ Priority: 29.07.89 JP 197050/89

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⑯ Date of publication of application:  
06.02.91 Bulletin 91/06

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⑯ Publication of the grant of the patent:  
18.10.95 Bulletin 95/42

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⑯ Designated Contracting States:  
DE FR GB

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1-18-1, Nishiaraisakaecho  
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DATABASE WPIL, accession no. 6879553P,  
Derwent Publications Ltd., London, GB; & JP  
- A - 422935

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**Description****BACKGROUND OF THE INVENTION****5 [Field of the Invention]**

The present invention relates to a hydrophilic polycarbodiimide polymer, a pulp-like material consisting of said hydrophilic polycarbodiimide polymer, and a process for producing said polymer or said material.

**10 [Prior Art]**

Polycarbodiimides, particularly aromatic polycarbodiimides are known to have high heat resistance and are used as a thermosetting molding material by, for example, subjecting them in a powder form to hot pressing.

15 Processes for producing a polycarbodiimide are disclosed in, for example, Japanese Patent Application Kokai (Laid-Open) No. 61599/1976; D. J. Lyman et al., "Die Makromol. Chem., 67, 1 (1963)"; and E. Dyer et al., "J. Am. Chem. Soc., 80, 5495 (1958)". In these processes, as the polymerization solvent, there are used hydrocarbons (e.g. benzene), o-dichlorobenzene, etc.; the monomer concentration is 10-25% by weight; and there are used, as the organic diisocyanate, 4,4'-diphenylmethane diisocyanate, tolylene diisocyanate and various other diisocyanates. The polycarbodiimides produced according to these processes have a powder form. In the above documents, mentioned is also made of a film produced by taking out the polymer from the reaction system after 10 minutes from the start of reaction and casting the polymer.

20 In the above known reaction, however, when the reaction time from the start of reaction exceeds 10 minutes, the reaction system causes gelation and precipitation and accordingly it is impossible to obtain the reaction product as a solution. That is, in the above processes, it is impossible to obtain a high-molecular polycarbodiimide solution having excellent stability.

Meanwhile, it is anticipated that imparting hydrophilicity to a polycarbodiimide will widen the application of the polycarbodiimide; to impart hydrophilicity to a polycarbodiimide, it is considered to adopt a method for introducing a quaternary ammonium salt into the main chain of the polycarbodiimide, which method is 30 already known and disclosed in Japanese Patent Publication No. 5118/1967 or Japanese Patent Publication No. 24194/1967. Production of a quaternary ammonium salt-containing polycarbodiimide by the above-mentioned known processes for polycarbodiimide production causes gelation and precipitation, and it is impossible to obtain an intended product, polycarbodiimide solution.

35 A polycarbodiimide solution can be obtained by suppressing a carbodiimidization reaction; however, the resulting polymer is not endowed with heat resistance which is a feature of polycarbodiimide, and has only about the same heat resistances that urethane has, which is a detrimental drawback.

From US-A-4 221 572 carbodiimides which do not contain quaternized nitrogen atoms are known.

Thus, there has hitherto been produced no hydrophilic polycarbodiimide.

**40 SUMMARY OF THE INVENTION.**

The present invention has been made in view of the above-mentioned problems of the prior art and provides a hydrophilic polycarbodiimide polymer, a pulp-like material consisting of said polymer, and a process for producing said polymer or said material.

45 To this end, the present invention provides the hydrophilic polycarbodiimide polymer characterized by being obtained by the method, comprising reacting an organic diisocyanate and an alkyliminodiol to introduce a tertiary amino group into the organic diisocyanate, converting the introduced tertiary amino group to a quaternary ammonium salt with a quaternizing agent, and then effecting carbodiimidization in the presence of a carbodiimidization catalyst, or by being obtained by the method, comprising at least partially 50 carbodiimidizing an organic diisocyanate in the presence of a carbodiimidization catalyst, reacting the resulting polycarbodiimide with an alkyliminodiol to introduce a tertiary amino group into the polycarbodiimide, and then converting the introduced tertiary amino group to a quaternary ammonium salt with a quaternizing agent.

The present invention also provides the pulp-like material consisting of a hydrophilic polycarbodiimide 55 polymer according to the present invention, characterized by being obtained by the method, comprising reacting an organic diisocyanate and an alkyliminodiol to introduce a tertiary amino group into the organic diisocyanate, converting the introduced tertiary amino group to a quaternary ammonium salt with a quaternizing agent, effecting carbodiimidization in the presence of a carbodiimidization catalyst to obtain a

5 hydrophilic polycarbodiimide polymer, and transferring the hydrophilic polycarbodiimide polymer into a poor solvent for the polymer while applying a shearing force, or by being obtained by the method, comprising at least partially carbodiimidizing an organic diisocyanate in the presence of a carbodiimidization catalyst, reacting the resulting polycarbodiimide with an alkyliminodiol to introduce a tertiary amino group into the polycarbodiimide, converting the introduced tertiary amino group to a quaternary ammonium salt with a quaternizing agent to obtain a hydrophilic polycarbodiimide polymer, and transferring the hydrophilic polycarbodiimide polymer into a poor solvent for the polymer while applying a shearing force.

10 The present invention also provides the process for producing a hydrophilic polycarbodiimide polymer, comprising reacting an organic diisocyanate and an alkyliminodiol to introduce a tertiary amino group into the organic diisocyanate, converting the introduced tertiary amino group to a quaternary ammonium salt with a quaternizing agent, and then effecting carbodiimidization in the presence of a carbodiimidization catalyst to obtain a hydrophilic polycarbodiimide polymer according to the present invention, or comprising at least partially carbodiimidizing an organic diisocyanate in the presence of a carbodiimidization catalyst, reacting the resulting polycarbodiimide with an alkyliminodiol to introduce a tertiary amino group into the polycarbodiimide, and then converting the introduced tertiary amino group to a quaternary ammonium salt with a quaternizing agent to obtain a hydrophilic polycarbodiimide polymer according to the present invention.

15 The present invention further provides the process for producing a pulp-like material consisting of a hydrophilic polycarbodiimide polymer, comprising reacting an organic diisocyanate and an alkyliminodiol to introduce a tertiary amino group into the organic diisocyanate, converting the introduced tertiary amino group to a quaternary ammonium salt with a quaternizing agent, effecting carbodiimidization in the presence of a carbodiimidization catalyst to obtain a hydrophilic polycarbodiimide polymer, and transferring the hydrophilic polycarbodiimide polymer into a poor solvent for the polymer while applying a shearing force, to obtain a pulp-like material consisting of a hydrophilic polycarbodiimide polymer according to the present invention, or comprising at least partially carbodiimidizing an organic diisocyanate in the presence of a carbodiimidization catalyst, reacting the resulting polycarbodiimide with an alkyliminodiol to introduce a tertiary amino group into the polycarbodiimide, converting the introduced tertiary amino group to a quaternary ammonium salt with a quaternizing agent to obtain a hydrophilic polycarbodiimide polymer, and transferring the hydrophilic polycarbodiimide polymer into a poor solvent for the polymer while applying a shearing force, to obtain a pulp-like material consisting of a hydrophilic polycarbodiimide polymer according to the present invention.

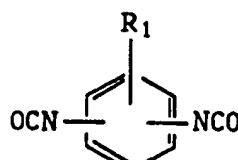
#### DESCRIPTION OF PREFERRED EMBODIMENTS

20 35 The present invention is described in detail below.

In order to obtain a hydrophilic polycarbodiimide of this invention, first an organic diisocyanate and an alkyliminodiol are reacted to introduce a tertiary amino group into the organic diisocyanate. In this reaction, the organic diisocyanate as a raw material includes, for example, those represented by the formula

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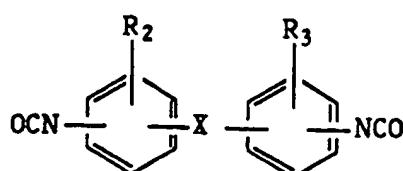
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(R1 represents a lower alkyl group or a lower alkoxy group)  
or by the formula

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(R<sub>2</sub> and R<sub>3</sub> each represent a hydrogen atom, a lower alkyl group or a lower alkoxy group, and X represents an oxygen atom or a methylene group).

As the alkyliminodiol, there is used, for example, a compound represented by the formula

5 R-N-(R'-OH)<sub>2</sub>

(R represents a lower alkyl group and R' represents an alkylene group, a polyalkylene group or an oxyalkylene group of 1-10 carbon atoms).

In the above reaction, the concentration of the organic diisocyanate is set at 1-50% by weight, 10 preferably 5-40% by weight (when expressed in viscosity at 25 °C, for example, 10-1,000cps, preferably 20-500cps); and the alkyliminodiol is used in an amount of about 1/10 to 1/50 equivalent per the amount of the organic diisocyanate. When the amount of the alkyliminodiol is more than 1/10 equivalent, the resulting polycarbodiimide polymer has low heat resistance. When the amount is less than 1/50 equivalent, the resulting polycarbodiimide polymer shows no pulping and becomes granular or gel-like lumps.

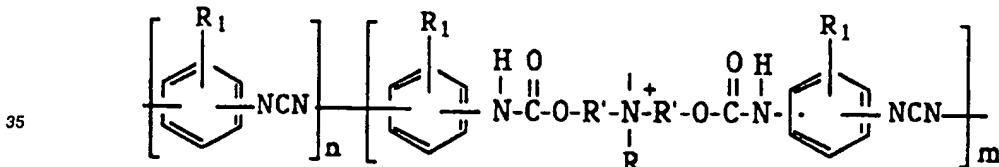
15 The above reaction is effected in an alicyclic ether. Specific examples of the alicyclic ether are tetrahydrofuran, dioxane, tetrahydropyran and their mixed solvents.

Next, the resulting organic diisocyanate having a tertiary amino group therein is treated with a quaternizing agent to convert the tertiary amino group to a quaternary ammonium salt. As the quaternizing agent, there can be mentioned known compounds such as dimethyl sulfate, methyl halides.

20 Thereafter, carbodiimidization is effected in the presence of a carbodiimidization catalyst to obtain a hydrophilic polycarbodiimide polymer of the present invention. As the carbodiimidization catalyst, there can be used known compounds, i. e., phosphorene oxides such as 1-phenyl-2-phosphorene-1-oxide, 3-methyl-2-phosphorene-1-oxide, 1-ethyl-3-methyl-2-phosphorene-1-oxide, 1-ethyl-2-phosphorene-1-oxide and their 3-phosphorene isomers.

25 The thus obtained polycarbodiimide polymer of the present invention has a quaternary ammonium salt in the main chain and accordingly is hydrophilic. The main structure of the polycarbodiimide polymer, when the polymer is produced from the above-mentioned starting materials, i. e. an organic diisocyanate and an alkyliminodiol, is represented by the formula

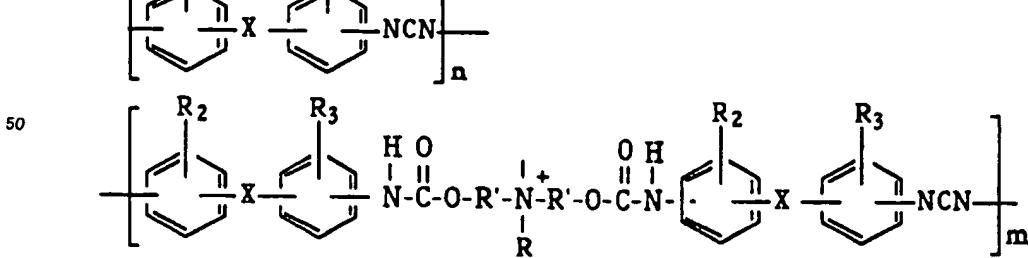
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(R<sub>1</sub> represents a lower alkyl group or a lower alkoxy group, R represents a lower alkyl group, and R'

40 represents an alkylene group, a polyalkylene group or an oxyalkylene group of 1-10 carbon atoms) or by the formula

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(R<sub>2</sub> and R<sub>3</sub> each represent a hydrogen atom, a lower alkyl group or a lower alkoxy group, X represents an oxygen atom or a methylene group, R represents a lower alkyl group, and R' represents an alkylene

group, a polyalkylene group or an oxyalkylene group of 1-10 carbon atoms).

Instead of the above process comprising introducing a tertiary amino group into an organic diisocyanate, converting the tertiary amino group to a quaternary ammonium salt with a quaternizing agent, and effecting carbodiimidization, the hydrophilic polycarbodiimide polymer of the present invention can also be produced by a process comprising at least partially carbodiimidizing an organic diisocyanate in the presence of a carbodiimidization catalyst to form a prepolymer (polycarbodiimide), reacting the prepolymer with an alkyliminodiol to introduce a tertiary amino group into the polycarbodiimide, then converting the tertiary amino group to a quaternary ammonium salt with a quaternizing agent.

The polycarbodiimide polymer of the present invention has a quaternary ammonium salt in the main chain and accordingly has hydrophilicity. Therefore, when it is placed in a poor solvent, the quaternary ammonium salt portion functions as an intramolecular surface-active agent, whereby the polycarbodiimide polymer easily becomes a pulp-like material. That is, the above obtained hydrophilic polycarbodiimide polymer is transferred into a poor solvent for the polymer while applying a shearing force, whereby a pulp-like material consisting of the hydrophilic polycarbodiimide polymer of the present invention can be produced.

In that case, the hydrophilic polycarbodiimide polymer may be any of those produced according to the above two processes; the poor solvent is most economically water; and the shearing force is applied most easily by stirring.

The above process for producing the pulp-like material belongs to the fibrid process which has conventionally been used in pulping a polyester or a polyamide. The fibrid process has not been applied to polymers of very low solubility such as polycarbodiimide, because in the case of these polymers it has been impossible to prepare a dope solution in order to enable the use of the fibrid process.

From the standpoint of application on industrial scale, the fibrid process has not been applied even to a polyester, a polyamide, etc. because the control of poor solvent solution is complicated and incurs a high cost.

#### [Advantage of the Invention]

Thus, the hydrophilic polycarbodiimide polymer of the present invention has a quaternary ammonium salt in the main chain and resultantly has hydrophilicity; accordingly, when it is placed in a poor solvent, the quaternary ammonium salt portion functions as an intramolecular surface-active agent, and the polymer easily becomes a pulp-like material. The use of a water-soluble alicyclic ether as the solvent also contributes to said pulping.

The thus obtained pulp-like material retains heat resistance intrinsically possessed by polycarbodiimide and also has a thermosetting property; therefore, it can be made into a sheet by itself, or can be used in paper making as a reinforcing agent, and thus can find various useful applications.

The present invention is described in more detail below by way of Examples and Comparative Examples.

#### 40 Example 1

800 g of methylenediphenyl diisocyanate (hereinafter referred to as MDI) was added to 2,000 ml of tetrahydrofuran (hereinafter referred to as THF). Thereto was added 13 g of methyl iminodiethanol, and the mixture was subjected to a reaction. Then, 13.5 g of dimethyl sulfate was added as a quaternizing agent to effect quaternization.

To the resulting solution was added a carbodiimidization catalyst, and a reaction was effected at 67°C for 4 hours. The resulting polymer solution was poured into water of about 10-fold volume while applying a shearing force, to obtain a pulp-like material.

The pulp-like material had the following properties.

Freeness:	744 ml (JIS P 8121)
Weight-average fiber length	0.8-1.0 mm (95% or more) (JIS P 8207)
Thermal decomposition temperature:	400°C

Examples 2-8

The pulp-like materials were obtained by using hydrophilic polycarbodiimide solutions produced in the same manner as Example 1 under the conditions shown in Table 1. The thermal decomposition temperatures of thus obtained pulp-like materials are shown in Table 2.

Comparative Example 1

The hydrophilic polycarbodiimide solution was produced in the same manner as Example 1 under the conditions shown in Table 1. Thus obtained hydrophilic polycarbodiimide solution was poured into water of about 10-fold volume while applying a shearing force in the same manner as Example 1. However, no pulp-like material was obtained, and instead a precipitate of granular form was obtained. The thermal decomposition temperature of thus obtained precipitate of granular form is shown in Table 2.

Comparative Example 2

The reaction was effected in the same manner as Example 1 under the conditions shown in Table 1. However, a precipitate was formed in the middle of the reaction, i.e., when the carbodiimidization catalyst was added. No pulp-like material was obtained. The thermal decomposition temperature of thus formed precipitate is shown in Table 2.

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Table I

	Organic diisocyanate	Solvent	Alkyliniiodiol	Quaternizing Agent	Reaction time (hr)
Example2	MDI (800 g)	THF (2 L)	Methyliniiodiethanol (25 g)	Dimethyl sulfate (27 g)	4
Example3	MDI (800 g)	THF (2 L)	Methyliniiodiethanol (8 g)	Dimethyl sulfate (8.5 g)	4
Example4	MDI (600 g)	THF (3.9 L)	Methyliniiodiethanol (10.2 g)	Dimethyl sulfate (10.8 g)	6
Example5	TDI (600 g)	THF (1.6 L)	Methyliniiodiethanol (13.7 g)	Methyl iodide (39 g)	7
Example6	TDI (600 g)	Dioxane (1.5 L, 100°C)	Methyliniodopropanol (15.3 g)	Methyl iodide (39 g)	3.5
Example7	EDI (110 g)	THF (640 mL)	Ethyliniiodiethanol (2.0 g)	Methyl iodide (3.0 g)	6
Example8	MDI (100 g)	THF (640 mL)	Methyliniiodiethanol (17 g)	Methyl iodide (2.5 g)	6.5
Comparative Example1	MDI (800 g)	THF (2 L)	Methyliniiodiethanol (76 g)	Dimethyl sulfate (81 g)	4
Comparative Example2	MDI (800 g)	Toluene (2 L)	Methyliniiodiethanol (25 g)	Dimethyl sulfate (27 g)	4

In the above table, MDI refers to methylenediphenyl diisocyanate; TDI refers to a mixture of 2,4-toluylene diisocyanate and 2,6-toluylene diisocyanate; and EDI refers to 4,4'-diphenylether diisocyanate.

Table 2

	Freeness:	Weight-average fiber length:	Thermal decomposition temperature (°C)	
5	Example 2	726	0.54 - 0.81	390
	Example 3	760	1.0 - 1.2	405
10	Example 4	730	0.8 - 1.0	400
	Example 5	720	0.35 - 0.50	390
	Example 6	730	0.45 - 0.70	385
	Example 7	760	1.0 - 1.2	405
15	Example 8	725	0.60 - 0.80	400
	Comparative Example 1	-	-	290
	Comparative Example 2	-	-	300

## Example 9

20 800 g of MDI was added to 2,000 ml of THF. Thereto was added a carbodiimidization catalyst. The mixture was subjected to a reaction at 67 °C for 5 hours. The system was returned cooled to room temperature, 13 g of methyl iminodiethanol was added, and a reaction was effected for 2 hours. Then, 13.5 g of dimethyl sulfate was added to effect quaternization. The resulting solution was poured into water of 13-fold volume while applying a shearing force, to obtain a pulp-like material.

25 The properties of the pulp-like material were as follows (the same test methods as in Example 1 were used).

Freeness:	763 ml
Weight-average fiber length:	1.0-1.2 mm.
Thermal decomposition temperature:	400 °C

## Example 10

35 800 g of MDI was added to 2,500 ml of THF. Thereto was added 13 g of methyl iminodiethanol, and a reaction was effected. 12 g of methyl chloride was introduced by bubbling while the system was vigorously stirred. Then, a carbodiimidization catalyst was added and a reaction was effected at 67 °C for 4 hours. The resulting solution was poured into water of 13-fold volume while applying a shearing force, to obtain a pulp-like material.

40 The pulp-like material had the following properties (the same test methods as in Example were used).

Freeness:	744 ml
Weight-average fiber length:	1.0-1.2 mm
Thermal decomposition temperature:	400 °C

## Claims

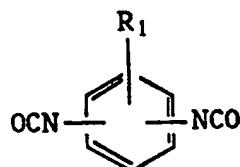
50 1. A hydrophilic polycarbodiimide polymer characterized by being obtained by the method, comprising reacting an organic diisocyanate and an alkyliminodiol whereby alkyliminodiol is used in an amount of 1/10 to 1/50 equivalent per the amount of the organic diisocyanate and whereby the reaction is effected in alicyclic ether as solvent to introduce a tertiary amino group into the organic diisocyanate, converting the introduced tertiary amino group to a quaternary ammonium salt with a quaternizing agent, and then effecting carbodiimidization in the presence of a carbodiimidization catalyst.

55 2. A hydrophilic polycarbodiimide polymer characterized by being obtained by the method, comprising at least partially carbodiimidizing an organic diisocyanate in the presence of a carbodiimidization catalyst,

reacting in resulting polycarbodiimide with an alkyliminodiol whereby alkyliminodiol is used in an amount of 1/10 to 1/50 equivalent per the amount of the organic diisocyanate and whereby the reaction is effected in alicyclic ether as solvent to introduce a tertiary amino group into the polycarbodiimide, and then converting the introduced tertiary amino group to a quaternary ammonium salt with a quaternizing agent.

3. A hydrophilic polycarbodiimide polymer according to Claim 1 or 2, wherein the organic diisocyanate is represented by the formula

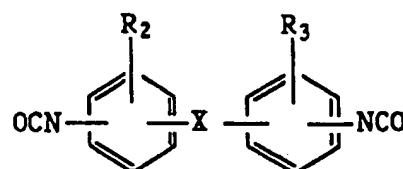
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(R<sub>1</sub> represents a lower alkyl group or a lower alkoxy group)  
or by the formula

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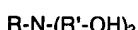


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(R<sub>2</sub> and R<sub>3</sub> each represent a hydrogen atom, a lower alkyl group or a lower alkoxy group, and X represents an oxygen atom or a methylene group).

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4. A hydrophilic polycarbodiimide polymer according to claim 1 or 2, wherein the alkyliminodiol is represented by the formula

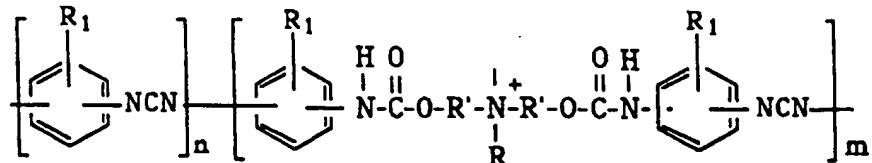


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(R represents a lower alkyl group and R' represents an alkylene group, a polyalkylene group or an oxyalkylene group of 1-10 carbon atoms)

5. A hydrophilic polycarbodiimide polymer according to Claim 3 or 4, which has a main structure represented by the formula

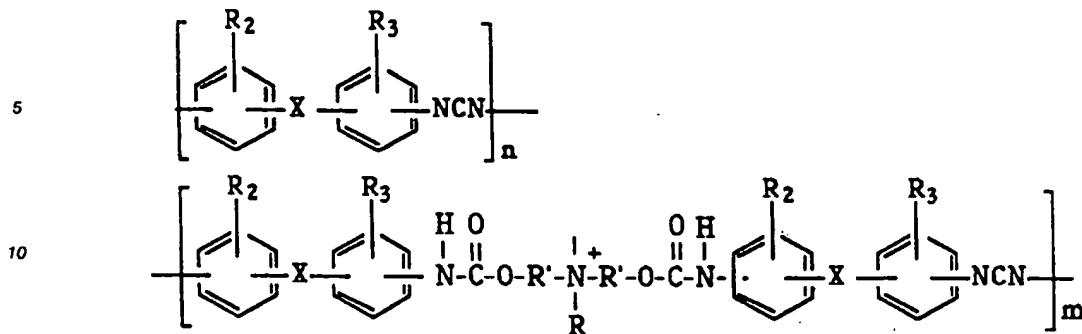
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(R<sub>1</sub> represents a lower alkyl group or a lower alkoxy group, R represents a lower alkyl group, and R' represents an alkylene group, a polyalkylene group or an oxyalkylene group of 1-10 carbon atoms) or by the formula

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6. A pulp-like material consisting of a hydrophilic polycarbodiimide polymer, characterized by being obtained by the method, comprising reacting an organic diisocyanate and an alkyliminodiol whereby alkyliminodiol is used in an amount of 1/10 to 1/50 equivalent per the amount of the organic diisocyanate and whereby the reaction is effected in alicyclic ether as solvent to introduce a tertiary amino group into the organic diisocyanate, converting the introduced tertiary amino group to a quaternary ammonium salt with a quaternizing agent, effecting carbodiimidization in the presence of a carbodiimidization catalyst to obtain a hydrophilic polycarbodiimide polymer, and transferring the hydrophilic polycarbodiimide polymer into a poor solvent for the polymer while applying a shearing force.

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7. A pulp-like material consisting of a hydrophilic polycarbodiimide polymer, characterized by being obtained by the method, comprising at least partially carbodiimidizing an organic diisocyanate in the presence of a carbodiimidization catalyst, reacting the resulting polycarbodiimide with an alkyliminodiol whereby alkyliminodiol is used in an amount of 1/10 to 1/50 equivalent per the amount of the organic diisocyanate and whereby the reaction is effected in alicyclic ether as solvent to introduce a tertiary amino group into the polycarbodiimide, converting the introduced tertiary amino group to a quaternary ammonium salt with a quaternizing agent to obtain a hydrophilic polycarbodiimide polymer, and transferring the hydrophilic polycarbodiimide polymer into a poor solvent for the polymer while applying a shearing force.

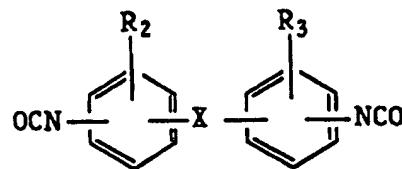
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8. A pulp-like material consisting of a hydrophilic polycarbodiimide polymer according to Claim 6 or 7, wherein the organic diisocyanate is represented by the formula



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(R<sub>1</sub> represents a lower alkyl group or a lower alkoxy group) or by the formula



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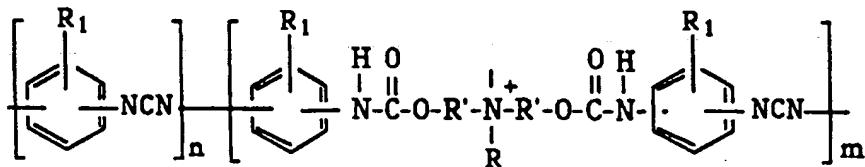
10 (R<sub>2</sub> and R<sub>3</sub> each represent a hydrogen atom, a lower alkyl group or a lower alkoxy group, and X represents an oxygen atom or a methylene group).

9. A pulp-like material consisting of a hydrophilic polycarbodiimide polymer according to Claim 6 or 7, wherein the alkyliminodiol is represented by the formula

15 R-N-(R'-OH)<sub>2</sub>

(R represents a lower alkyl group and R' represents an alkylene group, a polyalkylene group or an oxyalkylene group of 1-10 carbon atoms)

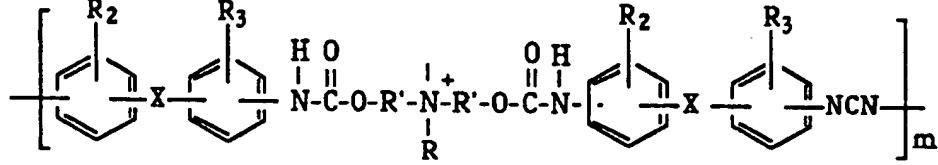
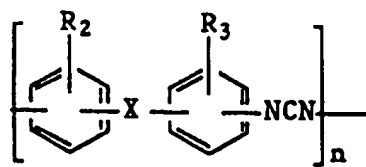
20 10. A pulp-like material consisting of a hydrophilic polycarbodiimide polymer according to Claim 8 or 9, wherein the hydrophilic polycarbodiimide polymer has a main structure represented by the formula



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(R<sub>1</sub> represents a lower alkyl group or a lower alkoxy group, R represents a lower alkyl group, and R' represents an alkylene group, a polyalkylene group or an oxyalkylene group of 1-10 carbon atoms) or by the formula

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( $R_2$  and  $R_3$  each represent a hydrogen atom, a lower alkyl group or a lower alkoxy group,  $X$  represents an oxygen atom or a methylene group,  $R$  represents a lower alkyl group, and  $R'$  represents an alkylene group, a polyalkylene group or an oxyalkylene group of 1-10 carbon atoms).

55 11. A pulp-like material consisting of a polycarbodiimide polymer according to Claim 6 or 7, wherein the poor solvent is water.

12. A process for producing a hydrophilic polycarbodiimide polymere, consisting of reacting an organic diisocyanate and an alkyliminodiol whereby alkyliminodiol is used in an amount of 1/10 to 1/50 equivalent per the amount of the organic diisocyanate and whereby the reaction is effected in alicyclic ether as solvent to introduce a tertiary amino group into the organic diisocyanate, converting the introduced tertiary amino group to a quaternary ammonium salt with a quaternizing agent, and then effecting carbodiimidization in the presence of a carbodiimidization catalyst.

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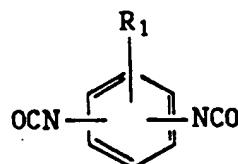
13. A process for producing a hydrophilic polycarbodiimide polymer, comprising at least partially carbodiimidizing an organic diisocyanate in the presence of a carbodiimidization catalyst, reacting the resulting polycarbodiimide with an alkyliminodiol whereby alkyliminodiol is used in an amount of 1/10 to 1/50 equivalent per the amount of the organic diisocyanate and whereby the reaction is effected in alicyclic ether as solvent to introduce a tertiary amino group into the polycarbodiimide, and then converting the introduced tertiary amino group to a quaternary ammonium salt with a quaternizing agent.

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14. A process for producing a hydrophilic polycarbodiimide polymer according to Claim 12 or 13, wherein the organic diisocyanate is represented by the formula

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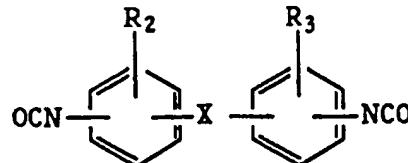
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(R<sub>1</sub> represents a lower alkyl group or a lower alkoxy group)  
or by the formula

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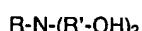
(R<sub>2</sub> and R<sub>3</sub> each represent a hydrogen atom, a lower alkyl group or a lower alkoxy group, and X represents an oxygen atom or a methylene group).

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15. A process for producing a hydrophilic polycarbodiimide polymer according to Claim 12 or 13, wherein the concentration of the organic diisocyanate is 5-40% by weight.

16. A process for producing a hydrophilic polycarbodiimide polymer according to Claim 12 or 13, wherein the alkyliminodiol is represented by the formula

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50 (R represents a lower alkyl group and R' represents an alkylene group, a polyalkylene group or an oxyalkylene group of 1-10 carbon atoms).

17. A process for producing a hydrophilic polycarbodiimide polymer according to Claim 12 or 13, wherein the alkyliminodiol is used in an amount of 1/10 to 1/50 equivalent per the amount of the organic diisocyanate.

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18. A process for producing a hydrophilic polycarbodiimide polymer according to Claim 12 or 13, wherein in the carbodiimidization, an alicyclic ether is used as the solvent.

19. A process for producing a hydrophilic polycarbodiimide polymer according to Claim 18, wherein the alicyclic ether is tetrahydrofuran, dioxane, tetrahydropyran or their mixture.

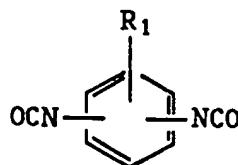
20. A process for producing a pulp-like material consisting of a hydrophilic polycarbodiimide polymer, comprising reacting an organic diisocyanate and an alkyliminodiol whereby alkyliminodiol is used in an amount of 1/10 to 1/50 equivalent per the amount of the organic diisocyanate and whereby the reaction is effected in alicyclic ether as solvent to introduce a tertiary amino group into the organic diisocyanate, converting the introduced tertiary amino group to a quaternary ammonium salt with a quaternizing agent, effecting carbodiimidization in the presence of a carbodiimidization catalyst to obtain a hydrophilic polycarbodiimide polymer, and transferring the hydrophilic polycarbodiimide polymer into a poor solvent for the polymer while applying a shearing force.

21. A process for producing a pulp-like material consisting of a hydrophilic polycarbodiimide polymer, comprising at least partially carbodiimidizing an organic diisocyanate in the presence of a carbodiimidization catalyst, reacting the resulting polycarbodiimide with an alkyliminodiol whereby alkyliminodiol is used in an amount of 1/10 to 1/50 equivalent per the amount of the organic diisocyanate and whereby the reaction is effected in alicyclic ether as solvent to introduce a tertiary amino group into the polycarbodiimide, converting the introduced tertiary amino group to a quaternary ammonium salt with a quaternizing agent to obtain a hydrophilic polycarbodiimide polymer, and transferring the hydrophilic polycarbodiimide polymer into a poor solvent for the polymer while applying a shearing force.

22. A process for producing a pulp-like material consisting of a hydrophilic polycarbodiimide polymer according to claim 20 or 21, wherein the organic diisocyanate is represented by the formula

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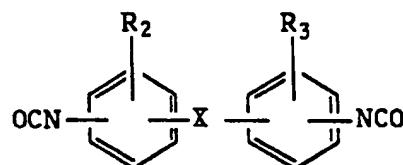
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(R<sub>1</sub> represents a lower alkyl group or a lower alkoxy group)  
or by the formula

40



45

(R<sub>2</sub> and R<sub>3</sub> each represent a hydrogen atom, a lower alkyl group or a lower alkoxy group, and X represents an oxygen atom or a methylene group).

50

23. A process for producing a pulp-like material consisting of a hydrophilic polycarbodiimide polymer according to Claim 20 or 21, wherein the concentration of the organic diisocyanate is 5-40% by weight.

24. A process for producing a pulp-like material consisting of a hydrophilic polycarbodiimide polymer according to Claim 20 or 21, wherein the alkyliminodiol is represented by the formula

55

R-N-(R'-OH)<sub>2</sub>

(R represents a lower alkyl group and R' represents an alkylene group, a polyalkylene group or an oxyalkylene group of 1-10 carbon atoms).

25. A process for producing a pulp-like material consisting of a hydrophilic polycarbodiimide polymer according to Claim 20 or 21, wherein the alkyliminodiol is used in an amount of 1/10 to 1/50 equivalent per the amount of the organic diisocyanate.

5 26. A process for producing a pulp-like material consisting of a hydrophilic polycarbodiimide polymer according to Claim 20 or 21, wherein in the carbodiimidization, an alicyclic ether is used as the solvent.

27. A process for producing a pulp-like material consisting of a hydrophilic polycarbodiimide polymer according to Claim 26, wherein the alicyclic ether is tetrahydrofuran, dioxane, tetrahydropyran or their mixture.

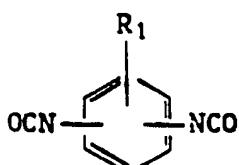
10 28. A process for producing a pulp-like material consisting of a hydrophilic polycarbodiimide polymer according to Claim 20 or 21, wherein the poor solvent is water.

## 15 Patentansprüche

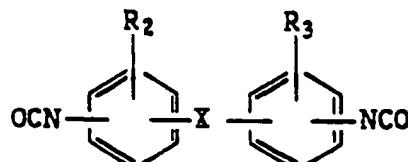
1. Hydrophiles Polycarbodiimidpolymer, dadurch gekennzeichnet, daß es mittels eines Verfahrens erhalten wird, welches das Umsetzen eines organischen Diisocyanats und eines Alkyliminodiols, wobei das Alkyliminodiol in einer Menge von 1/10 bis 1/50 Äquivalent pro Menge des organischen Diisocyanats verwendet wird und wobei die Reaktion in alicyclischem Äther als Lösungsmittel vorgenommen wird, um eine teriäre Aminogruppe in das organische Diisocyanat einzuführen, das Umwandeln der eingeführten teriären Aminogruppe in ein quaternäres Ammoniumsalz mit einem Quaterniermittel, und anschließend das Bewirken der Carbodiimidisation in Gegenwart eines Carbodiimidisations-Katalysators umfaßt.

20 2. Hydrophiles Polycarbodiimidpolymer, dadurch gekennzeichnet, daß es mittels eines Verfahrens erhalten wird, welches die zumindest teilweise Carbodiimidisation eines organischen Diisocyanats in Gegenwart eines Carbodiimidisations-Katalysators, das Umsetzen des resultierenden Polycarbodiimids mit einem Alkyliminodiol, wobei das Alkyliminodiol in einer Menge von 1/10 bis 1/50 Äquivalent pro Menge des organischen Diisocyanats verwendet wird und wobei die Reaktion in alicyclischem Äther als Lösungsmittel vorgenommen wird, um eine teriäre Aminogruppe in das Polycarbodiimid einzuführen, und anschließend das Umwandeln der eingeführten teriären Aminogruppe in ein quaternäres Ammoniumsalz mit einem Quaterniermittel umfaßt.

25 3. Hydrophiles Polycarbodiimidpolymer nach Anspruch 1 oder 2, worin das organische Diisocyanat dargestellt ist durch die Formel

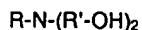


45 (R<sub>1</sub> steht für eine niedere Alkylgruppe oder eine niedere Alkoxygruppe) oder durch die Formel



55 (R<sub>2</sub> und R<sub>3</sub> stehen jeweils für ein Wasserstoffatom, eine niedere Alkylgruppe oder eine niedere Alkoxygruppe und X steht für ein Sauerstoffatom oder eine Methylengruppe).

4. Hydrophiles Polycarbodiimidpolymer nach Anspruch 1 oder 2, worin das Alkyliminodiol dargestellt ist durch die Formel



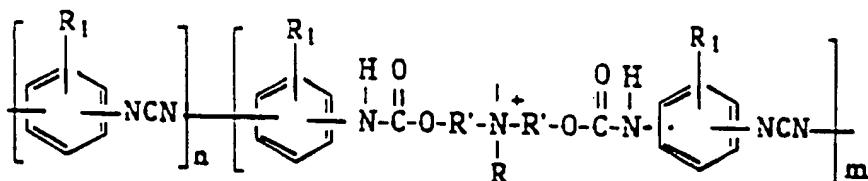
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(R steht für eine niedere Alkylgruppe und R' steht für eine Alkylengruppe, eine Polyalkylengruppe oder eine Oxyalkylengruppe mit 1-10 Kohlenstoffatomen).

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5. Hydrophiles Polycarbodiimidpolymer nach Anspruch 3 oder 4, dessen Hauptstruktur dargestellt ist durch die Formel

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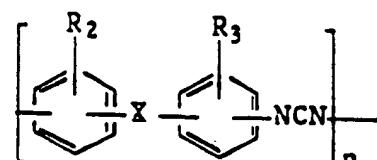
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(R<sub>1</sub> steht für eine niedere Alkylgruppe oder eine niedere Alkoxygruppe, R steht für eine niedere Alkylgruppe und R' steht für eine Alkylengruppe, eine Polyalkylengruppe oder eine Oxyalkylengruppe mit 1-10 Kohlenstoffatomen)

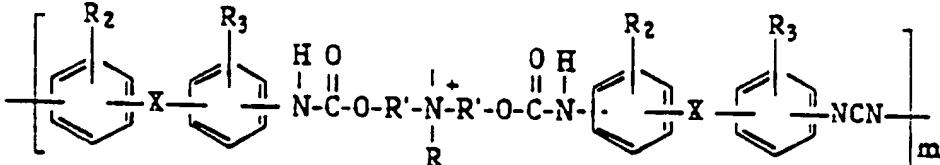
oder durch die Formel

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(R<sub>2</sub> und R<sub>3</sub> stehen jeweils für ein Wasserstoffatom, eine niedere Alkylgruppe oder eine niedere Alkoxygruppe, X steht für ein Sauerstoffatom oder eine Methylengruppe, R steht für eine niedere Alkylgruppe und R' steht für eine Alkylengruppe, eine Polyalkylengruppe oder eine Oxyalkylengruppe mit 1-10 Kohlenstoffatomen).

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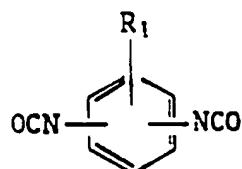
6. Pulpeartiges Material, bestehend aus einem hydrophilen Polycarbodiimidpolymer, dadurch gekennzeichnet, daß es mittels eines Verfahrens erhalten wird, welches das Umsetzen eines organischen Diisocyanats und eines Alkyliminodiols, wobei das Alkyliminodiol in einer Menge von 1/10 bis 1/50 Äquivalent pro Menge des organischen Diisocyanats verwendet wird und wobei die Reaktion in alicyclischem Äther als Lösungsmittel vorgenommen wird, um eine teriäre Aminogruppe in das organische Diisocyanat einzuführen, das Umwandeln der eingeführten teriären Aminogruppe in ein quaternäres Ammoniumsalz mit einem Quaterniermittel, das Bewirken der Carbodiimidisation in Gegenwart eines Carbodiimidisations-Katalysators, um ein hydrophiles Polycarbodiimidpolymer zu erhalten, und das Einbringen des hydrophilen Polycarbodiimidpolymers in ein schwaches Lösungsmittel für das Polymer unter Anlegen einer Scherkraft umfaßt.

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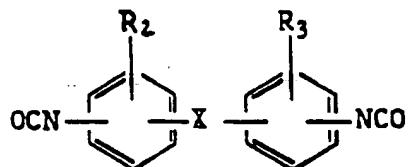
7. Pulpeartiges Material, bestehend aus einem hydrophilen Polycarbodiimidpolymer, dadurch gekennzeichnet, daß es mittels eines Verfahrens erhalten wird, welches die zumindest teilweise Carbodiimidisation eines organischen Diisocyanats in Gegenwart eines Carbodiimidisations-Katalysators, das Umset-

zen des resultierenden Polycarbodiimids mit einem Alkyliminodiol, wobei das Alkyliminodiol in einer Menge von 1/10 bis 1/50 Äquivalent pro Menge des organischen Diisocyanats verwendet wird und wobei die Reaktion in alicyclischem Äther als Lösungsmittel vorgenommen wird, um eine teriäre Aminogruppe in das Polycarbodiimid einzuführen, das Umwandeln der eingeführten tertären Aminogruppe in ein quaternäres Ammoniumsalz mit einem Quaterniermittel, um ein hydrophiles Polycarbodiimidpolymer zu erhalten, und das Einbringen des hydrophilen Polycarbodiimidpolymers in ein schwaches Lösungsmittel für das Polymer unter Anlegen einer Scherkraft umfaßt.

5 8. Pulpeartiges Material, bestehend aus einem hydrophilen Polycarbodiimidpolymer nach Anspruch 6 oder  
10 7, worin das organische Diisocyanat dargestellt ist durch die Formel

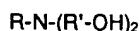


20 (R<sub>1</sub> steht für eine niedere Alkylgruppe oder eine niedere Alkoxygruppe) oder durch die Formel



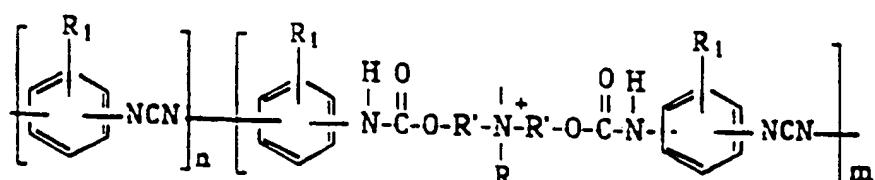
30 (R<sub>2</sub> und R<sub>3</sub> stehen jeweils für ein Wasserstoffatom, eine niedere Alkylgruppe oder eine niedere Alkoxygruppe und X steht für ein Sauerstoffatom oder eine Methylengruppe).

35 9. Pulpeartiges Material, bestehend aus einem hydrophilen Polycarbodiimidpolymer nach Anspruch 6 oder 7, worin das Alkyliminodiol dargestellt ist durch die Formel

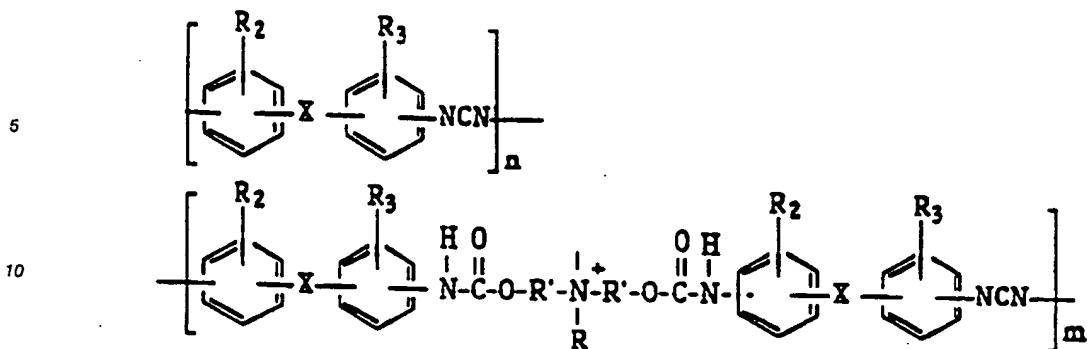


40 (R steht für eine niedere Alkylgruppe und R' steht für eine Alkylengruppe, eine Polyalkylengruppe oder eine Oxyalkylengruppe mit 1-10 Kohlenstoffatomen).

45 10. Pulpeartiges Material, bestehend aus einem hydrophilen Polycarbodiimidpolymer nach Anspruch 8 oder 9, worin das hydrophile Polycarbodiimidpolymer eine Hauptstruktur aufweist, dargestellt durch die Formel



55 (R<sub>1</sub> steht für eine niedere Alkylgruppe oder eine niedere Alkoxygruppe, R steht für eine niedere Alkylgruppe und R' steht für eine Alkylengruppe, eine Polyalkylengruppe oder eine Oxyalkylengruppe mit 1-10 Kohlenstoffatomen) oder durch die Formel



15 (R<sub>2</sub> und R<sub>3</sub> stehen jeweils für ein Wasserstoffatom, eine niedere Alkylgruppe oder eine niedere Alkoxygruppe, X steht für ein Sauerstoffatom oder eine Methylengruppe, R steht für eine niedere Alkylgruppe und R' steht für eine Alkylengruppe, eine Polyalkylengruppe oder eine Oxyalkylengruppe mit 1-10 Kohlenstoffatomen).

20 11. Pulpeartiges Material, bestehend aus einem hydrophilen Polycarbodiimidpolymer nach Anspruch 6 oder 7, worin das schwache Lösungsmittel Wasser ist.

25 12. Verfahren zur Herstellung eines hydrophilen Polycarbodiimidpolymers, welches das Umsetzen eines organischen Diisocyanats und eines Alkyliminodiols, wobei das Alkyliminodiol in einer Menge von 1/10 bis 1/50 Äquivalent pro Menge des organischen Diisocyanats verwendet wird und wobei die Reaktion in alicyclischem Äther als Lösungsmittel vorgenommen wird, um eine teriäre Aminogruppe in das organische Diisocyanat einzuführen, das Umwandeln der eingeführten teriären Aminogruppe in ein quaternäres Ammoniumsalz mit einem Quaterniermittel, und das anschließende Bewirken der Carbodiimidisation in Gegenwart eines Carbodiimidisations-Katalysators umfaßt.

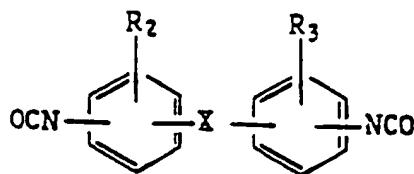
30 13. Verfahren zur Herstellung eines hydrophilen Polycarbodiimidpolymer, welches die zumindest teilweise Carbodiimidisation eines organischen Diisocyanats in Gegenwart eines Carbodiimidisations-Katalysators, das Umsetzen des resultierenden Polycarbodiimid mit einem Alkyliminodiol, wobei das Alkyliminodiol in einer Menge von 1/10 bis 1/50 Äquivalent pro Menge des organischen Diisocyanats verwendet wird und wobei die Reaktion in alicyclischem Äther als Lösungsmittel vorgenommen wird, um eine teriäre Aminogruppe in das Polycarbodiimid einzuführen, und anschließend das Umwandeln der eingeführten teriären Aminogruppe in ein quaternäres Ammoniumsalz mit einem Quaterniermittel umfaßt.

40 14. Verfahren zur Herstellung eines hydrophilen Polycarbodiimidpolymers nach Anspruch 12 oder 13, worin das organische Diisocyanat dargestellt ist durch die Formel



50 (R<sub>1</sub> steht für eine niedere Alkylgruppe oder eine niedere Alkoxygruppe) oder durch die Formel

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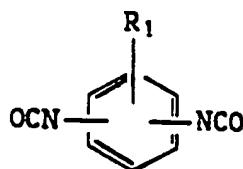


(R<sub>2</sub> und R<sub>3</sub> stehen jeweils für ein Wasserstoffatom, eine niedere Alkylgruppe oder eine niedere Alkoxygruppe und X steht für ein Sauerstoffatom oder eine Methylengruppe).

15. Verfahren zur Herstellung eines hydrophilen Polycarbodiimidpolymers nach Anspruch 12 oder 13, worin die Konzentration des organischen Diisocyanats 5-40 Gew.-% beträgt.
16. Verfahren zur Herstellung eines hydrophilen Polycarbodiimidpolymers nach Anspruch 12 oder 13, worin das Alkyliminodiol dargestellt ist durch die Formel
 
$$R-N-(R'-OH)_2$$

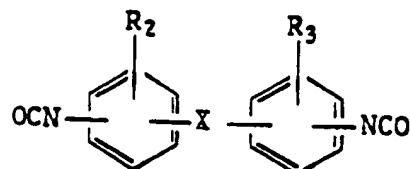
(R steht für eine niedere Alkylgruppe und R' steht für eine Alkylengruppe, eine Polyalkylengruppe oder eine Oxyalkylengruppe mit 1-10 Kohlenstoffatomen).
17. Verfahren zur Herstellung eines hydrophilen Polycarbodiimidpolymers nach Anspruch 12 oder 13, worin das Alkyliminodiol in einer Menge von 1/10 bis 1/50 Äquivalent pro Menge des organischen Diisocyanats verwendet wird.
18. Verfahren zur Herstellung eines hydrophilen Polycarbodiimidpolymers nach Anspruch 12 oder 13, worin bei der Carbodiimidisation ein alicyclischer Äther als das Lösungsmittel verwendet wird.
19. Verfahren zur Herstellung eines hydrophilen Polycarbodiimidpolymers nach Anspruch 18, worin der alicyclische Äther Tetrahydrofuran, Dioxan, Tetrahydropyran oder deren Gemische ist.
20. Verfahren zur Herstellung eines pulpeartigen Materials, bestehend aus einem hydrophilen Polycarbodiimidpolymer, welches das Umsetzen eines organischen Diisocyanats und eines Alkyliminodiols umfaßt, wobei das Alkyliminodiol in einer Menge von 1/10 bis 1/50 Äquivalent pro Menge des organischen Diisocyanats verwendet wird und wobei die Reaktion in alicyclischem Äther als Lösungsmittel vorgenommen wird, um eine tertiäre Aminogruppe in das organische Diisocyanat einzuführen, das Umwandeln der eingeführten tertiären Aminogruppe in ein quaternäres Ammoniumsalz mit einem Quaterniermittel, das Bewirken der Carbodiimidisation in Gegenwart eines Carbodiimidisations-Katalysators, um ein hydrophiles Polycarbodiimidpolymer zu erhalten, und das Einbringen des hydrophilen Polycarbodiimidpolymers in ein schwaches Lösungsmittel für das Polymer unter Anlegen einer Scherkraft umfaßt.
21. Verfahren zur Herstellung eines pulpeartigen Materials, bestehend aus einem hydrophilen Polycarbodiimidpolymer, welches die zumindest teilweise Carbodiimidisation eines organischen Diisocyanats in Gegenwart eines Carbodiimidisations-Katalysators, das Umsetzen des resultierenden Polycarbodiimids mit einem Alkyliminodiol, wobei das Alkyliminodiol in einer Menge von 1/10 bis 1/50 Äquivalent pro Menge des organischen Diisocyanats verwendet wird und wobei die Reaktion in alicyclischem Äther als Lösungsmittel vorgenommen wird, um eine tertiäre Aminogruppe in das Polycarbodiimid einzuführen, das Umwandeln der eingeführten tertiären Aminogruppe in ein quaternäres Ammoniumsalz mit einem Quaterniermittel, um ein hydrophiles Polycarbodiimidpolymer zu erhalten, und das Einbringen des hydrophilen Polycarbodiimidpolymers in ein schwaches Lösungsmittel für das Polymer unter Anlegen einer Scherkraft umfaßt.
22. Verfahren zur Herstellung eines pulpeartigen Materials, bestehend aus einem hydrophilen Polycarbodiimidpolymer nach Anspruch 20 oder 21, worin das organische Diisocyanat dargestellt ist durch die Formel

5



(R<sub>1</sub> steht für eine niedere Alkylgruppe oder eine niedere Alkoxygruppe)  
 10 oder durch die Formel

15



20 (R<sub>2</sub> und R<sub>3</sub> stehen jeweils für ein Wasserstoffatom, eine niedere Alkylgruppe oder eine niedere Alkoxygruppe und X steht für ein Sauerstoffatom oder eine Methylengruppe).

23. Verfahren zur Herstellung eines pulpeartigen Materials, bestehend aus einem hydrophilen Polycarbodiimidpolymer nach Anspruch 20 oder 21, worin die Konzentration des organischen Diisocyanats 5-40 Gew.-% beträgt.

24. Verfahren zur Herstellung eines pulpeartigen Materials, bestehend aus einem hydrophilen Polycarbodiimidpolymer nach Anspruch 20 oder 21, worin das Alkyliminodiol dargestellt ist durch die Formel

30 R-N-(R'-OH)<sub>2</sub>

(R steht für eine niedere Alkylgruppe und R' steht für eine Alkylengruppe, eine Polyalkylengruppe oder eine Oxyalkylengruppe mit 1-10 Kohlenstoffatomen).

35 25. Verfahren zur Herstellung eines pulpeartigen Materials, bestehend aus einem hydrophilen Polycarbodiimidpolymer nach Anspruch 20 oder 21, worin das Alkyliminodiol in einer Menge von 1/10 bis 1/50 Äquivalent pro Menge des organischen Diisocyanats verwendet wird.

40 26. Verfahren zur Herstellung eines pulpeartigen Materials, bestehend aus einem hydrophilen Polycarbodiimidpolymer nach Anspruch 20 oder 21, worin bei der Carbodiimidisation ein alicyclischer Äther als das Lösungsmittel verwendet wird.

45 27. Verfahren zur Herstellung eines pulpeartigen Materials, bestehend aus einem hydrophilen Polycarbodiimidpolymer nach Anspruch 26, worin der alicyclische Äther Tetrahydrofuran, Dioxan, Tetrahydropyran oder deren Gemische ist.

28. Verfahren zur Herstellung eines pulpeartigen Materials, bestehend aus einem hydrophilen Polycarbodiimidpolymer nach Anspruch 20 oder 21, worin das schwache Lösungsmittel Wasser ist.

#### 50 Revendications

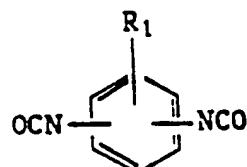
1. Polymère de polycarbodiimide hydrophile caractérisé en ce qu'il est obtenu par la méthode, comprenant la réaction d'un diisocyanate organique et d'un alkyliminodiol où l'alkyliminodiol est utilisé en une quantité de 1/10 à 1/50 d'équivalent par quantité de diisocyanate organique et où la réaction est effectuée dans un éther alicyclique en tant que solvant pour introduire un groupe amino tertiaire dans le diisocyanate organique, la conversion du groupe amino tertiaire introduit en un sel ammonium quaternaire avec un agent de quaternisation, et ensuite la réalisation de la carbodiimidisation en présence d'un catalyseur de carbodiimidisation.

2. Polymère polycarbodiimide hydrophile caractérisé en ce qu'il est obtenu par la méthode, comprenant la carbodiimidisation au moins partiellement d'un diisocyanate organique en présence d'un catalyseur de carbodiimidisation, la réaction dans le polycarbodiimide résultant avec un alkyliminodiol où l'alkyliminodiol est utilisé en une quantité de 1/10 à 1/50 d'équivalent par quantité du diisocyanate organique et où la réaction est effectuée dans un éther alicyclique en tant que solvant pour introduire un groupe amino tertiaire dans le polycarbodiimide, et ensuite la conversion du groupe amino tertiaire introduit en un sel d'ammonium quaternaire avec un agent de quaternisation.

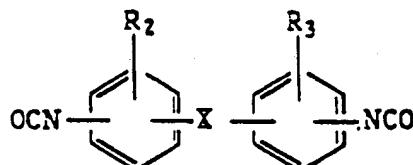
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3. Polymère de polycarbodiimide hydrophile selon la revendication 1 ou 2, dans lequel l'édit isocyanate organique est représenté par la formule

10



20 (R<sub>1</sub> représente un groupe alkyle inférieur ou un groupe alcoxy inférieur) ou par la formule



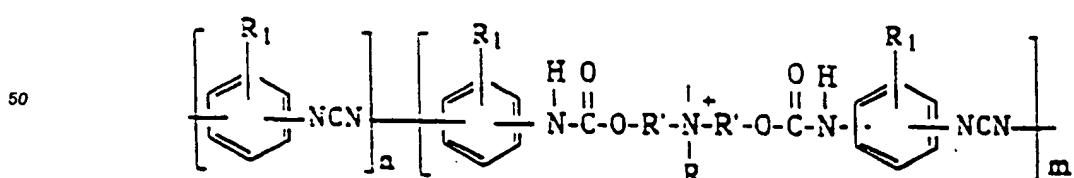
(R<sub>2</sub> et R<sub>3</sub> représentent chacun un atome hydrogène, un groupe alkyle inférieur ou un groupe alcoxy inférieur, et X représente un atome d'hydrogène ou un groupe méthylène).

35 4. Polymère de polycarbodiimide hydrophile selon la revendication 1 ou 2, où l'alkyliminodiol est représenté par la formule



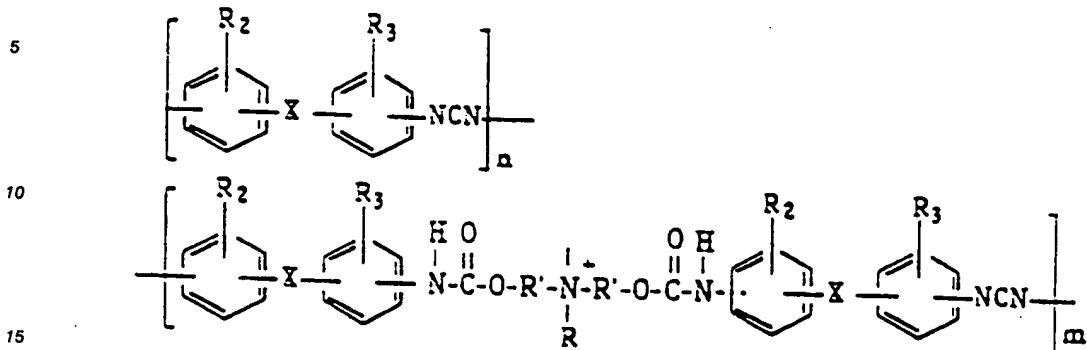
40 (R représente un groupe alkyle inférieur et R' représente un groupe alkylène, un groupe polyalkylène ou un groupe oxyalkylène de 1 à 10 atomes de carbone).

45 5. Polymère de carbodiimide hydrophile selon la revendication 3 ou 4, qui a une structure principale représentée par la formule



55 (R<sub>1</sub> représente un groupe alkyle inférieur ou un groupe alcoxy inférieur, R représente un groupe alkyle inférieur, et R' représente un groupe alkylène, un groupe polyalkylène ou groupe oxyalkylène de 1 à 10 atomes de carbone).

ou par la formule



(R<sub>2</sub> et R<sub>3</sub> représentent chacun un atome d'hydrogène, un groupe alkyle inférieur ou un groupe alcoxy inférieur, X représente un atome d'oxygène ou un groupe méthylène, R représente un groupe alkyle inférieur, et R' représente un groupe alkylène, un groupe polyalkylène ou un groupe oxyalkylène de 1 à 10 atomes de carbone).

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6. Matériau analogue à une pulpe consistant d'un polymère de polycarbodiimide hydrophile, caractérisé en ce qu'il est obtenu par la méthode, comprenant la réaction d'un diisocyanate organique et d'un alkyliminodiol où l'alkyliminodiol est utilisé en une quantité de 1/10 à 1/50 d'équivalent par quantité du diisocyanate organique et où la réaction est effectuée d'un éther alicyclique en tant que solvant pour introduire un groupe amino tertiaire dans le diisocyanate organique, la conversion du groupe amino tertiaire introduit en un sel d'ammonium quaternaire avec un agent de quaternisation, réalisation de la carbodiimidisation en présence d'un catalyseur de carbodiimidisation pour obtenir un polymère de polycarbodiimide hydrophile, et le transfert du polymère de polycarbodiimide hydrophile dans un solvant faible pour le polymère tout en appliquant une force de cisaillement.

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7. Matériau analogue à une pulpe consistant d'un polymère de polycarbodiimide hydrophile, caractérisé en ce qu'il est obtenu par la méthode, comprenant la carbodiimidisation au moins partiellement d'un diisocyanate organique en présence d'un catalyseur de carbodiimidisation, réaction du polycarbodiimide résultant avec un alkyliminodiol où l'alkyliminodiol est utilisé en une quantité de 1/10 à 1/50 d'équivalent par quantité du diisocyanate organique et où la réaction est effectuée dans un éther alicyclique en tant que solvant pour introduire un groupe aminotertiaire dans le polycarbodiimide, conversion du groupe amino tertiaire introduit en un sel ammonium quaternaire avec un agent de quaternisation pour obtenir un polymère de polycarbodiimide hydrophile et transfert du polymère de polycarbodiimide hydrophile dans un solvant faible pour le polymère tout en appliquant une force de cisaillement.

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8. Matériau analogue à une pulpe consistant d'un polymère de polycarbodiimide hydrophile selon la revendication 6 ou 7, où ledit isocyanate organique est représenté par la formule

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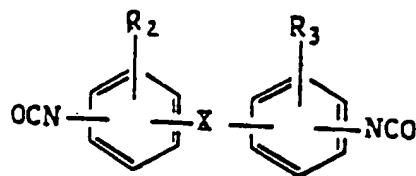
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(R<sub>1</sub> représente un groupe alkyle inférieur ou un groupe alcoxy inférieur)  
ou par la formule



10 (R<sub>2</sub> et R<sub>3</sub> représentent chacun un atome hydrogène, un groupe alkyle inférieur ou un groupe alcoxy inférieur, et X représente un atome d'hydrogène ou un groupe méthylène).

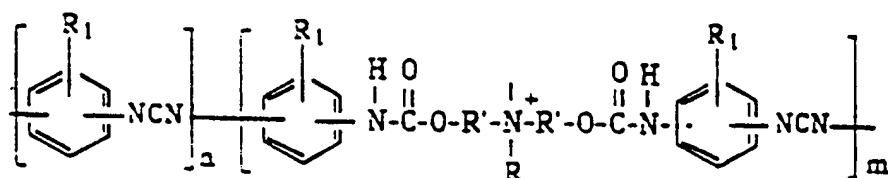
9. Matériau analogue à une pulpe consistant d'un polymère de polycarbodiimide hydrophile selon la revendication 6 ou 7, où l'alkyliminodiol est représenté par la formule

15 R-N-(R'-OH)<sub>2</sub>

(R représente un groupe alkyle inférieur et R' représente un groupe alkylène, un groupe polyalkylène ou un groupe oxyalkylène de 1 à 10 atomes de carbone).

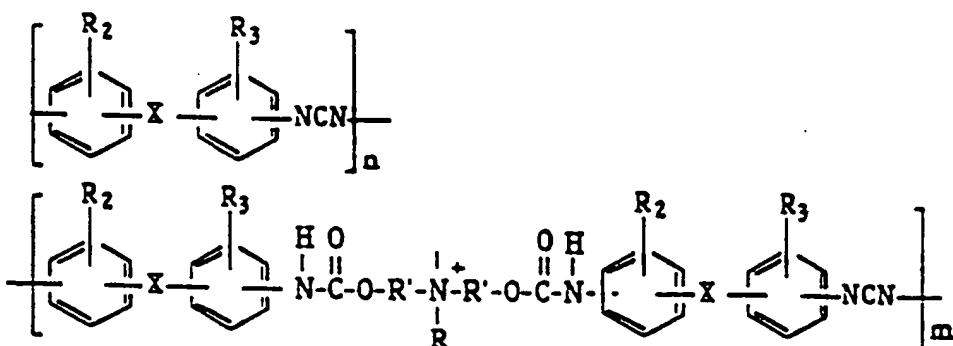
20 10. Matériau analogue à une pulpe consistant d'un polymère de polycarbodiimide hydrophile selon la revendication 8 ou 9, où le polymère de polycarbodiimide hydrophile a une structure principale représentée par la formule

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35 (R<sub>1</sub> représente un groupe alkyle inférieur ou un groupe alcoxy inférieur, R représente un groupe alkyle inférieur et R' représente un groupe alkylène, un groupe polyalkylène ou groupe oxyalkylène de 1 à 10 atomes de carbone) ou par la formule

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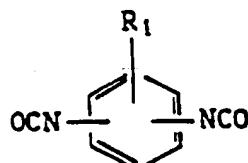
55 (R<sub>2</sub> et R<sub>3</sub> représentent chacun un atome d'hydrogène, un groupe alkyle inférieur ou un groupe alcoxy inférieur, X représente un atome d'oxygène ou un groupe méthylène, R représente un groupe alkyle inférieur, et R' représente un groupe alkylène, un groupe polyalkylène ou un groupe oxyalkylène de 1 à 10 atomes de carbone).

11. Matériau analogue à une pulpe consistant d'un polymère de polycarbodiimide selon la revendication 6 ou 7, où le solvant faible est l'eau.

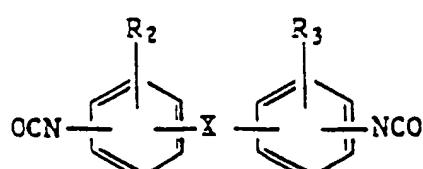
12. Procédé pour produire un polymère de carbodiimide hydrophile, consistant en la réaction d'un diisocyanate organique et d'un alkyliminodiol où l'alkyliminodiol est utilisé en une quantité de 1/10 à 1/50 équivalent par quantité de diisocyanate organique et où la réaction est effectuée dans un éther alicyclique en tant que solvant pour introduire un groupe amino tertiaire dans le diisocyanate organique, en la conversion du groupe amino tertiaire introduit en un sel ammonium quaternaire avec un agent de quaternisation, et ensuite en la réalisation de la carbodiimidisation en présence d'un catalyseur de carbodiimidisation.

13. Procédé pour produire un polymère de polycarbodiimide hydrophile, comprenant la carbodiimidisation au moins partiellement d'un diisocyanate organique en présence d'un catalyseur de carbodiimidisation, la réaction du polycarbodiimide résultant avec un alkyliminodiol où l'alkyliminodiol est utilisé en une quantité de 1/10 à 1/50 d'équivalent par quantité du diisocyanate organique et où la réaction est effectuée dans un éther alicyclique comme solvant pour introduire un groupe amino tertiaire dans le polycarbodiimide, et ensuite conversion du groupe amino tertiaire introduit en un sel d'ammonium quaternaire avec un agent de quaternisation.

14. Procédé pour produire un polymère de polycarbodiimide hydrophile selon la revendication 12 ou 13, où ledit isocyanate organique est représenté par la formule



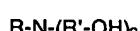
30 (R<sub>1</sub> représente un groupe alkyle inférieur ou un groupe alcoxy inférieur) ou par la formule



45 (R<sub>2</sub> et R<sub>3</sub> représentent chacun un atome d'hydrogène, un groupe alkyle inférieur ou un groupe alcoxy inférieur et X représente un atome d'oxygène ou un atome méthylène).

15. Procédé pour produire un polymère de polycarbodiimide hydrophile selon la revendication 12 ou 13, où la concentration du diisocyanate organique est de 5 à 40% en poids.

16. Procédé pour produire un polymère polycarbodiimide hydrophile selon la revendication 12 ou 13 où l'alkyliminodiol est représenté par la formule



55 (R représente un groupe alkyle inférieur et R' représente un groupe alkylène, un groupe polyalkylène ou un groupe oxyalkylène de 1 à 10 atomes de carbone).

17. Procédé pour produire un polymère de polycarbodiimide hydrophile selon la revendication 12 ou 13, où l'alkyliminodiol est utilisé en une quantité de 1/10 à 1/50 d'équivalent par quantité du diisocyanate organique.

5 18. Procédé pour produire un polymère de polycarbodiimide hydrophile selon la revendication 12 ou 13, où dans la carbodiimidisation, un éther alicyclique est utilisé comme solvant.

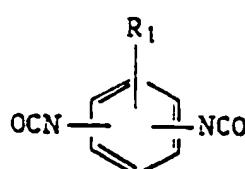
10 19. Procédé pour produire un polymère de polycarbodiimide hydrophile selon la revendication 18, où l'éther alicyclique est le tétrahydrofurane, le dioxane, le tétrahydropyrane ou leur mélange.

10 20. Procédé pour produire un matériau analogue à une pulpe consistant d'un polymère de polycarbodiimide hydrophile, comprenant la réaction d'un diisocyanate organique et d'un alkyliminodiol où l'alkyliminodiol est utilisé en une quantité de 1/10 à 1/50 d'équivalent par quantité du diisocyanate organique et où la réaction est effectuée dans un éther alicyclique comme solvant pour introduire un groupe amino tertiaire dans ledit isocyanate organique, la conversion du groupe amino tertiaire introduit en un sel d'ammonium quaternaire avec un agent de quaternisation, la réalisation de la carbodiimidisation en présence d'un catalyseur de carbodiimidisation pour obtenir un polymère polycarbodiimide hydrophile, et le transfert du polymère de polycarbodiimide hydrophile dans un solvant faible pour le polymère tout en appliquant une force de cisaillement.

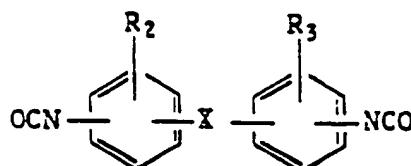
20 21. Procédé pour produire un matériau analogue à une pulpe consistant d'un polymère de carbodiimide hydrophile, comprenant la carbodiimidisation au moins partiellement d'un diisocyanate organique en présence d'un catalyseur de carbodiimidisation, la réaction du polycarbodiimide résultant avec un alkyliminodiol où l'alkyliminodiol est utilisé en une quantité de 1/10 à 1/50 d'équivalent par quantité du diisocyanate organique et où la réaction est effectuée dans un éther alicyclique comme solvant pour introduire un groupe amino tertiaire dans le polycarbodiimide, la conversion du groupe amino tertiaire introduit en un sel d'ammonium quaternaire avec un agent de quaternisation pour obtenir un polymère de polycarbodiimide hydrophile, et le transfert du polymère de polycarbodiimide hydrophile dans un solvant faible pour le polymère tout en appliquant une force de cisaillement.

25 22. Procédé pour produire un matériau analogue à une pulpe consistant d'un polymère de carbodiimide selon la revendication 20 ou 21, où ledit isocyanate organique est représenté par la formule

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(R<sub>1</sub> représente un groupe alkyle inférieur ou un groupe alcoxy inférieur)  
ou par la formule



(R<sub>2</sub> et R<sub>3</sub> représentent chacun un atome d'hydrogène, un groupe alkyle inférieur ou un groupe alcoxy inférieur, et X représente un atome d'oxygène ou un groupe méthylène).

23. Procédé pour produire un matériau analogue à une pulpe consistant d'un polymère de polycarbodiimide hydrophile selon la revendication 20 ou 21, où la concentration du diisocyanate organique est de 5 à 40% en poids.

5 24. Procédé pour produire un matériau analogue à une pulpe consistant d'un polymère de polycarbodiimide hydrophile selon la revendication 20 ou 21, où l'alkyliminodiol est représenté par la formule

R-N-(R'-OH)<sub>2</sub>

10 (R représente un groupe alkyle inférieur et R' représente un groupe alkylène, un groupe polyalkylène ou un groupe oxyalkylène de 1 à 10 atomes de carbone).

15 25. Procédé pour produire un matériau analogue à une pulpe consistant d'un polymère de polycarbodiimide hydrophile selon la revendication 20 ou 21, où l'alkyliminodiol est utilisé en une quantité de 1/10 à 1/50 d'équivalent par quantité du diisocyanate organique.

20 26. Procédé pour produire un matériau analogue à une pulpe consistant d'un polymère de polycarbodiimide hydrophile selon la revendication 20 ou 21, où dans la carbodiimidisation, un éther alicyclique est utilisé comme solvant.

27. Procédé pour produire un matériau analogue à une pulpe consistant d'un polymère de polycarbodiimide hydrophile selon la revendication 26, où l'éther alicyclique est du tétrahydrofurane, du dioxane, et du tétrahydropyrane ou leurs mélanges.

25 28. Procédé pour produire un matériau analogue à une pulpe consistant d'un polymère polycarbodiimide hydrophile selon la revendication 20 ou 21, où le solvant faible est l'eau.

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